

SECOND SEMIANNUAL REPORT

January 1, 1964 - June 1, 1964

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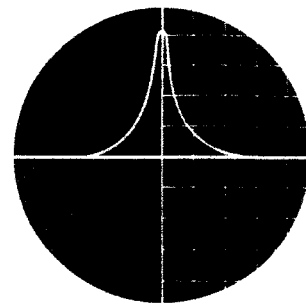
DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

By

Stuart A. Hoenig
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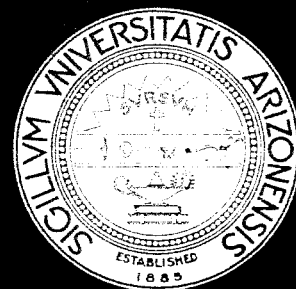
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To

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National Aeronautics and Space Administration
Washington, D. C., 20546

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SUMMARY

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A chemisorption detector for hydrogen has been developed. This device operates over the pressure range from 10^{-5} to 10^{-8} torr and has a large and repeatable response to hydrogen. The detector makes use of the effect of hydrogen chemisorption on the work function of a palladium filament. This system is reasonably specific for hydrogen, and the effect of oxygen and nitrogen has been investigated. Oxygen has a substantial effect, but nitrogen does not.

A similar detector for water vapor, using a barium coated tungsten filament, has been tested and is undergoing further development. The water vapor detector operates over the pressure range from 10^{-4} to 10^{-7} torr, at present, and is insensitive to nitrogen and oxygen.

The large (18 inch diameter) U-H-V molecular beam system has been finished and leak checked. The hydrogen furnace for production of atomic hydrogen has been finished and found to operate properly in its first tests.

Final installation of the atomic-hydrogen molecular beam system will be completed this fall when the new laboratory space is available.

Author

I. INTRODUCTION

This program was set up to investigate chemisorption phenomena with the ultimate aim of developing devices for the investigation of tenuous planetary atmospheres. Since the program, as originally proposed, involved several semi-independent studies, this report will be divided into several parts in order to discuss the work done in each of these areas.

II. CHEMISORPTION DETECTOR FOR HYDROGEN

Because of the well known reaction and rapid diffusion of hydrogen in palladium, this material was chosen for our first experiments. Highly purified palladium wire was used as a filament cathode in the diode arrangement shown in Fig. 1. The change in emission current from the palladium filament was measured as a function of the hydrogen pressure, under steady state conditions.

The results were encouraging, however it proved impossible to flash the palladium to completely remove chemisorbed gases, because of the low melting point of palladium (1552°C). To avoid these problems a supply of tungsten wire coated with 0.00002" thickness of palladium was ordered from Sigmund Cohn Corporation of New York. This material is now being tested, but does not seem to respond in the same manner as solid palladium wire. We hope to investigate the erratic behavior of palladium coated tungsten wire in some detail next year. It may be possible to increase the thickness of the palladium coating and achieve more repeatable results.

The response of the present solid-wire palladium detector is shown in Fig. 2. The hydrogen raises the work function when it is chemisorbed. This is in complete agreement with the work reported by Trapnell⁽¹⁾ for hydrogen chemisorption on other metals.

The response of the detector is shown for two separate filaments (at 1000°C) in the upper curves (A, B). Both filaments give essentially the same output at lower pressures, the spread at higher pressures is probably due to the differences in geometry between the two filaments. Since the filaments are welded in place by hand some changes in geometry from filament to filament are unavoidable.

The response of the detector at a higher filament temperature (1100°C) is shown in the lower curve. Higher temperatures lower the rate of chemisorption and therefore reduce the effective sensitivity of the detector. Conversely lower filament temperatures should increase sensitivity and we hope to gain some information about the optimum detector temperature in the coming year.

The effect of oxygen on the hydrogen detector is shown in Fig. 3. In this case the hydrogen pressure was held at a constant level while oxygen was added. The effect is a drastic one, the oxygen apparently displaces the hydrogen and then lowers the palladium work function. This would indicate that the detector could not be used in hydrogen/oxygen atmospheres. However, such atmospheres are very unlikely and this should be no real detriment to the use of the detector.

A hydrogen/nitrogen atmosphere is much more likely and the response of the detector to H_2/N_2 mixtures is shown in Fig. 4. Until rather large ratios of nitrogen to hydrogen are reached there is no appreciable effect of the nitrogen on the hydrogen detector. Since atmospheres containing H_2 , N_2 , CO , CO_2 and C_2H_2 are often suggested for the outer planets, we hope next year to run tests on the detector using these gases.

A paper covering this work will be submitted to the Review of Scientific Instruments in the coming summer.

III. CHEMISORPTION DETECTOR FOR WATER VAPOR

After some discussion with Dr. Donald Easter of the NASA Lunar and Planetary Programs Office, it was decided that a water vapor detector would be of most interest to NASA programs.

The existing water vapor detectors were investigated and it appeared that neither the phosphorous pentoxide (Beckman Instruments) nor the Quartz Oscillator (Gilbert & Barker Mfg. Co., West Springfield, Massachusetts) was sensitive at the pressures involved (10^{-6} torr). A search of the literature for a water vapor chemisorption reaction indicated that a barium coated filament might be used as a detector or an attempt could be made to use the tungsten-water cycle first suggested by Langmuir⁽²⁾.

Barium is a metal of the calcium group and when it is chemisorbed by tungsten there is a lowering of the effective tungsten work function. Any reaction which removed the barium from the tungsten would be detectable because the increase in effective work function would cause a drop in the emission current. Barium is known to chemisorb oxygen but without a change in work function,⁽³⁾ water vapor on the other hand reacts to form barium hydrates which are desorbed. To check on this a tungsten filament was coated with barium carbonate and placed in the U-H-V system. The wire was heated to 1090°C at 10^{-9} torr and then exposed to oxygen and nitrogen at various pressures up to 10^{-4} torr. No change in work function was noted.

The wire was then exposed to water vapor at pressures from about 10^{-8} to 10^{-4} torr. A change in emission current of a factor of 10^{+4} was noted indicating that this system will serve as a detector for water vapor in the vacuum regimen.

This work is being repeated and a better method for placing the barium on the tungsten is being tested. The introduction of water vapor

into the U-H-V system has been rather difficult; the walls of the vacuum system adsorb water, and some new components (valves, leaks, etc.) have had to be developed for this purpose.

Since massspectrometers do not measure water vapor accurately, we are still working on a system for measuring the actual water vapor pressure in the U-H-V system. Hot cathode ionization gauges are quickly destroyed by water⁽²⁾ and we have been measuring water vapor pressures by monitoring the Vac-Ion pump current. Since Vac-Ion pumps operate at different speeds with different gases, this method is rather uncertain. A careful search of the literature indicated that no good methods existed for measuring water vapor pressures in the 10^{-6} torr range. We will design a liquid-nitrogen-cooled-storage system and a calibrated capillary leak during the summer months.

IV. OXYGEN DETECTOR

The tests of the detector in CO_2/O_2 mixtures were finished and no effect of CO_2 was observed. The thoriated-tungsten oxygen detector has been redesigned for easier operation but no tests have been run because of the hydrogen detector work. These tests will be made in the new fiscal year starting June 1, probably by October 1964.

V. MOLECULAR BEAM SYSTEM

This was described in our previous report, manufacture is now complete and assembly will begin about August or September 1964 when the new laboratory space is ready. Experimental apparatus will be designed and built this summer. The atomic hydrogen furnace has been tested and found to operate as expected.

VI. FUTURE PLANS

We hope to investigate the hydrogen and water vapor detectors in greater detail and improve their sensitivity and reliability. One interesting effect of the oxygen reaction with palladium is that the sensitivity for detection of pure hydrogen is greatly increased after the filament has been exposed to oxygen. This may be a surface modification effect such as that reported for oxygen reacting with nickel⁽⁴⁾. More investigation will be needed before this technique can be used for improving the effective sensitivity of the hydrogen detector.

The large U-H-V system and the hydrogen atom furnace will be assembled this summer and fall. All the objectives of the first year of the program have been met with the exception of the large U-H-V system, which was expected to take more than one year for completion.

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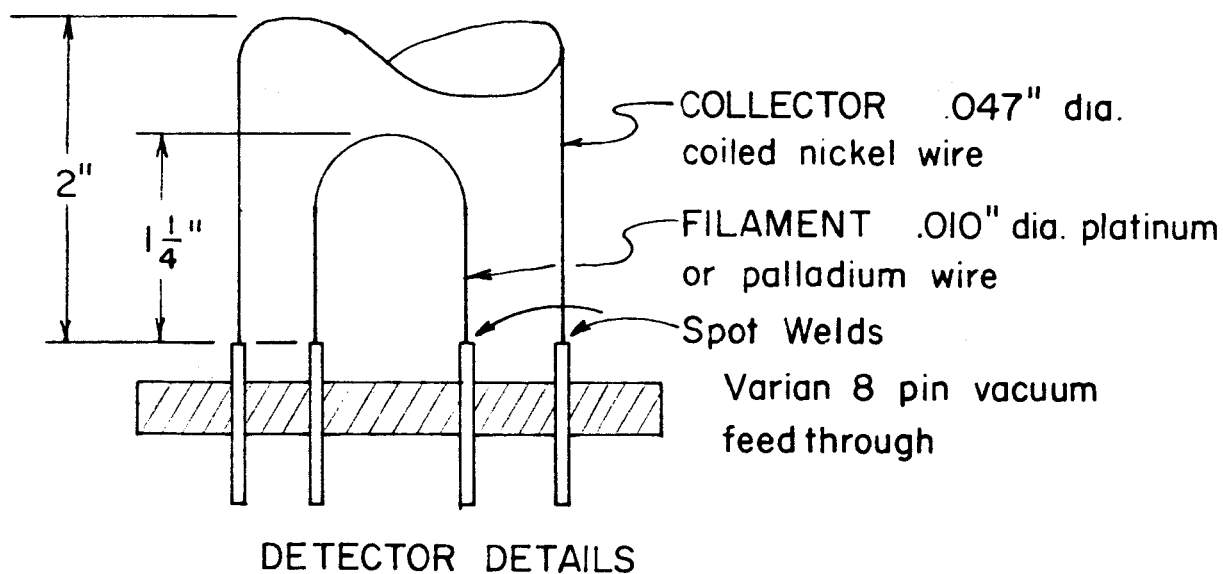
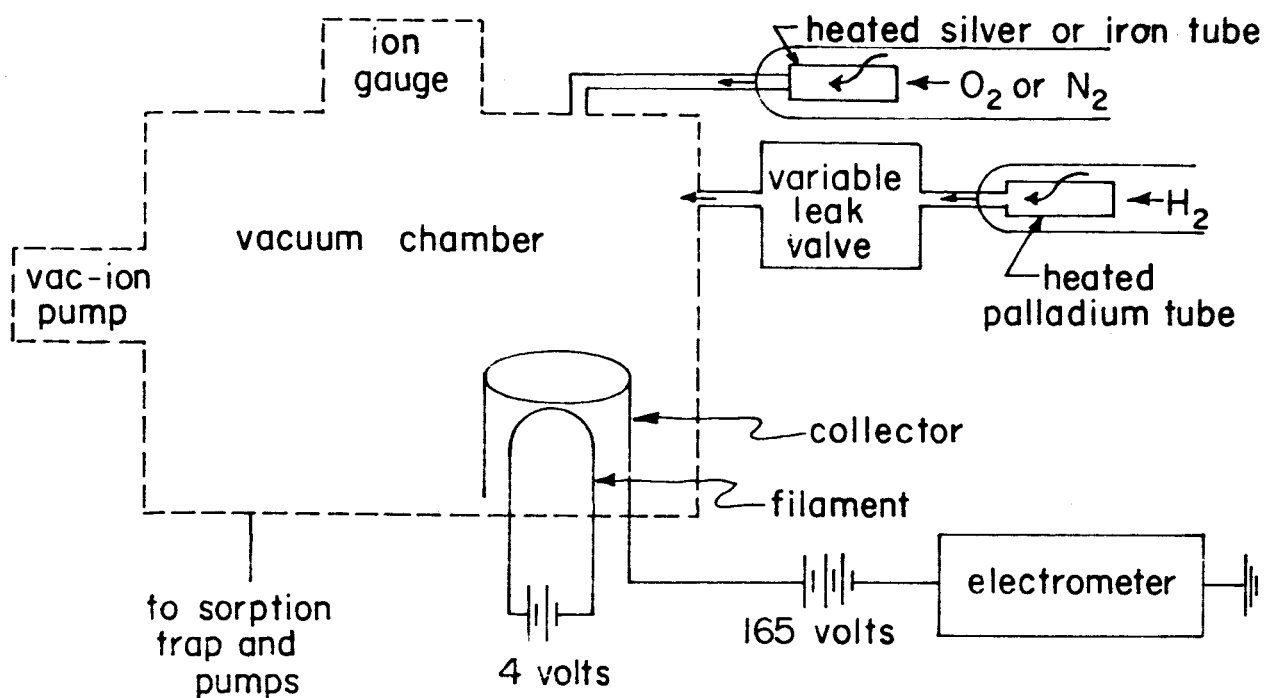


FIG. 1 EXPERIMENTAL SYSTEM

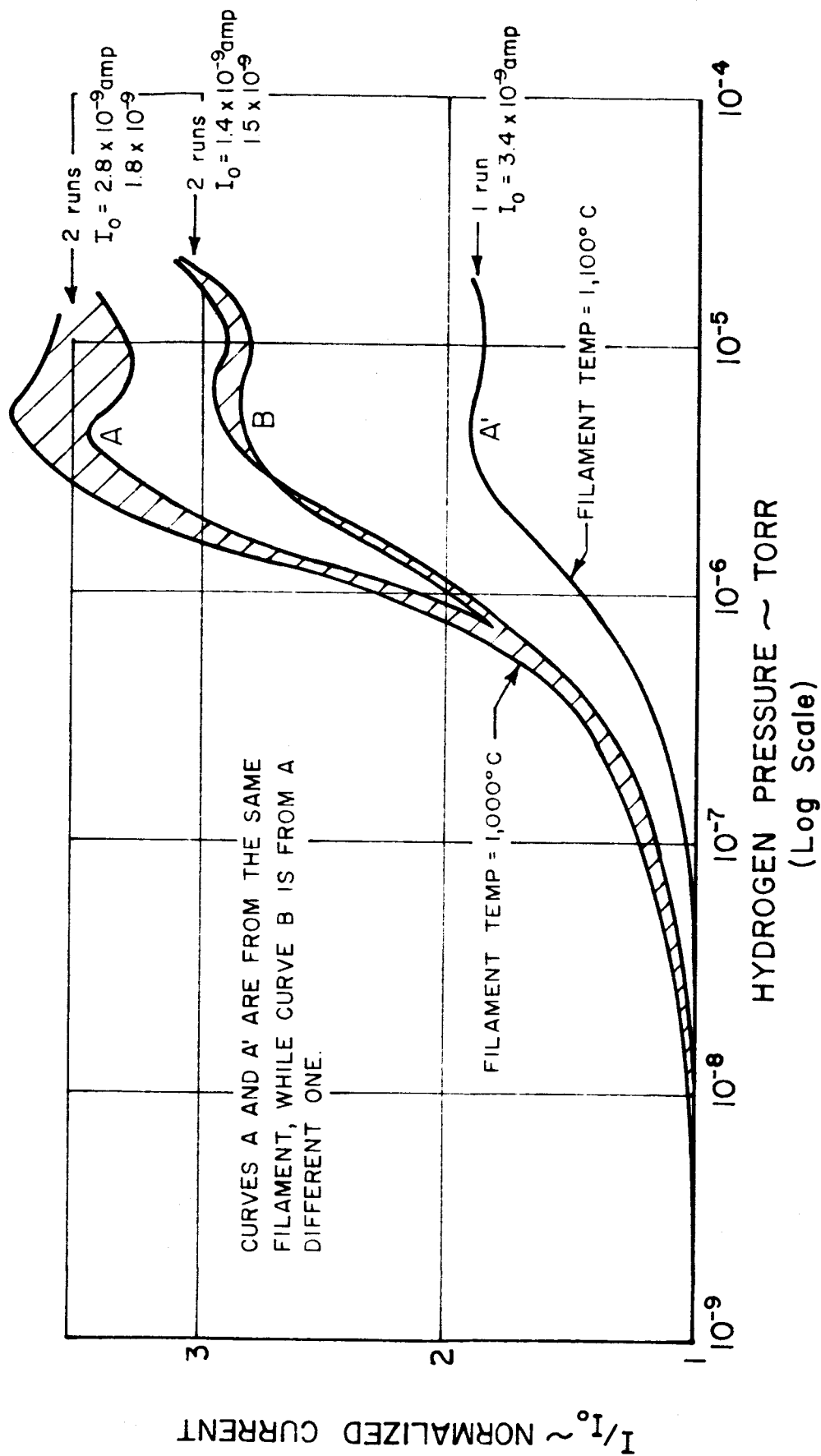


Figure 2. Normalized Emission Current vs. Hydrogen Pressure. Curve A shows the data obtained from 2 runs on one filament, at a filament temp of $1,000^\circ\text{C}$. The data spread is indicated by the diagonal lines. Curve B presents the data for two runs on a different filament, again at $1,000^\circ\text{C}$. Curve A' uses the same filament as curve A, however the filament was run at $1,100^\circ\text{C}$.

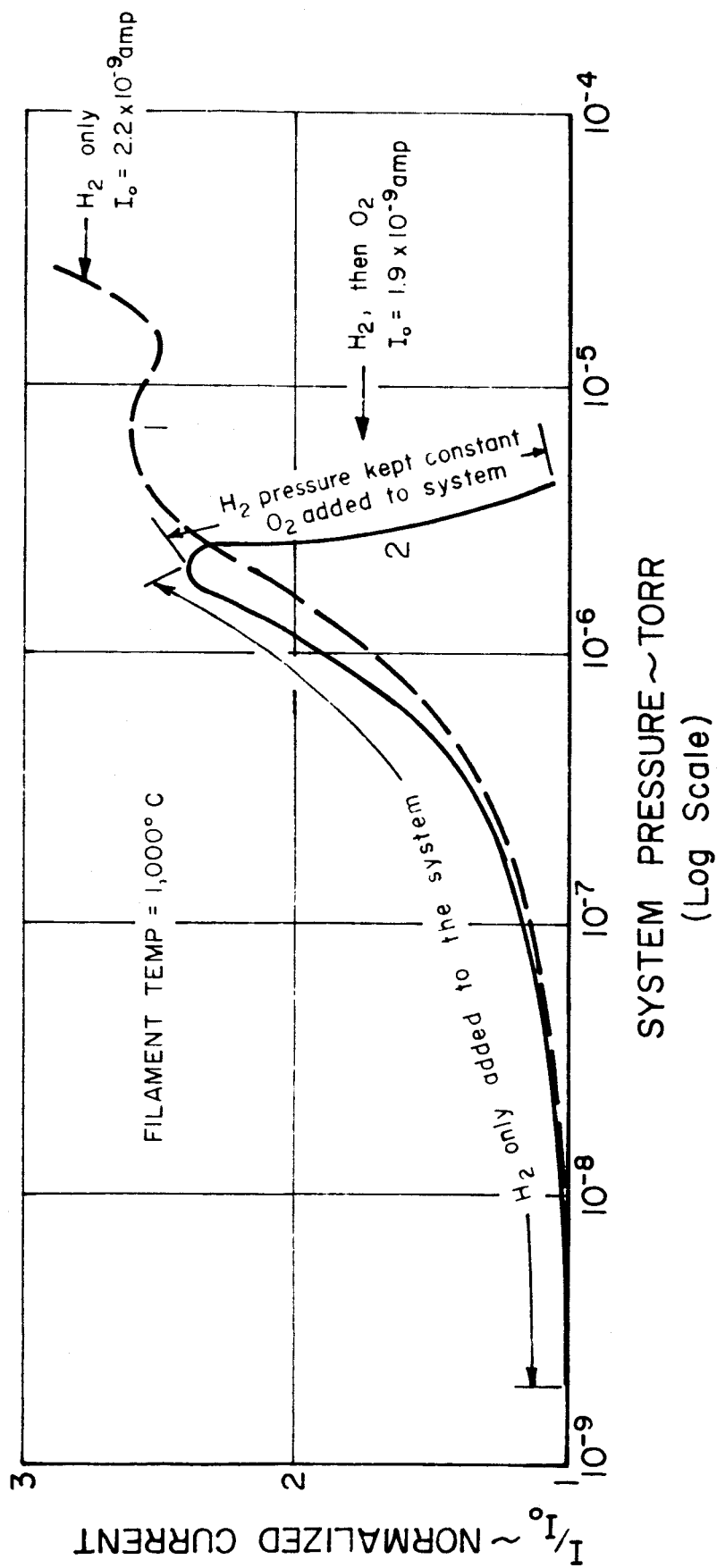


Figure 3. Effect of Oxygen on Detector Operation. Curve 1 shows the results of a hydrogen atmosphere. For curve 2, hydrogen was added until a system pressure of 2.1×10^{-6} torr prevailed. This hydrogen pressure was maintained, and O₂ was then admitted.

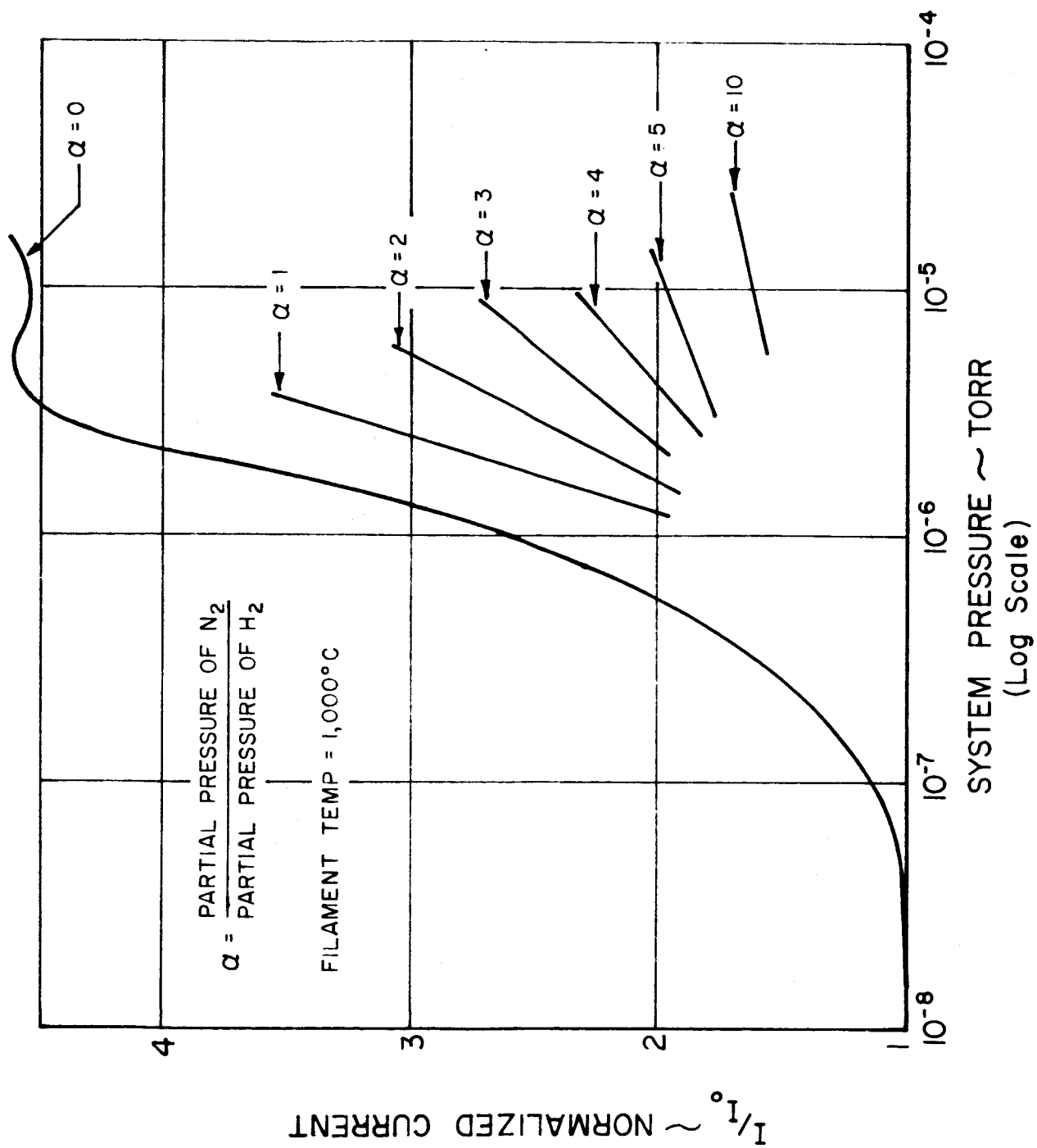


Figure 4. Effect of Nitrogen on Detector Operation.